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PTO/SB/05 (4/98)  
Approved for use through 09/30/2000. OMB 0651-0032  
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. 503.39144X00

First Inventor or Application Identifier Takeyuki ITABASHI, ET AL.

Title See 1 in Addendum

Express Mail Label No.

## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO:

Assistant Commissioner for Patents  
Box Patent Application  
Washington, DC 20231

1. ☒ \* Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 61]  
(preferred arrangement set forth below)
- Descriptive title of the Invention
  - Cross References to Related Applications
  - Statement Regarding Fed sponsored R & D
  - Reference to Microfiche Appendix
  - Background of the Invention
  - Brief Summary of the Invention
  - Brief Description of the Drawings (if filed)
  - Detailed Description
  - Claim(s)
  - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 5]
4. Oath or Declaration [Total Pages ]
- a. ☐ Newly executed (original or copy)
- b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))  
(for continuation/divisional with Box 16 completed)
- i. ☐ DELETION OF INVENTOR(S)  
Signed statement attached deleting  
inventor(s) named in the prior application,  
see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission  
(if applicable, all necessary)
- a. ☐ Computer Readable Copy
- b. ☐ Paper Copy (identical to computer copy)
- c. ☐ Statement verifying identity of above copies

## ACCOMPANYING APPLICATION PARTS

7. ☐ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement ☐ Power of  
(when there is an assignee) ☐ Attorney
9. ☐ English Translation Document (if applicable)
10. ☐ Information Disclosure ☐ Copies of IDS  
Statement (IDS)/PTO-1449 ☐ Citations
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)
13. ☐ \* Small Entity ☐ Statement filed in prior application  
Statement(s) ☐ Status still proper and desired  
(PTO/SB/09-12)
14. ☐ Certified Copy of Priority Document(s)  
(if foreign priority is claimed)
15. ☒ Other: List and copies of Prior Art References

\* NOTE FOR ITEMS 1 & 13 IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY  
FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT  
IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No. /  
Prior application information: Examiner Group / Art Unit:

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied  
under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by  
reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

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Name (Print/Type)	William I. Solomon	Registration No. (Attorney/Agent)	28,565
Signature	<i>William I. Solomon</i>	Date	10/04/2000

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Attachment to PTO/SB/05 (4/98) Utility Patent Application  
Transmittal

1. ELECTROLESS COPPER PLATING MACHINE THEREOF, AND MULTI-LAYER  
PRINTED WIRING BOARD

09678800-100400

<h1 style="margin: 0;">FEE TRANSMITTAL</h1> <h2 style="margin: 0;">for FY 2000</h2> <p style="font-size: small; margin: 0;">Patent fees are subject to annual revision Small Entity payments <u>must</u> be supported by a small entity statement, otherwise large entity fees must be paid. See Forms PTO/SB/09-12 See 37 C.F.R. §§ 1.27 and 1.28.</p>	<p><b>Complete if Known</b></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">Application Number</td> <td></td> </tr> <tr> <td>Filing Date</td> <td>October 4, 2000</td> </tr> <tr> <td>First Named Inventor</td> <td>Takeyuki ITABASHI, ET AL.</td> </tr> <tr> <td>Examiner Name</td> <td></td> </tr> <tr> <td>Group / Art Unit</td> <td></td> </tr> <tr> <td>Attorney Docket No.</td> <td>503.39144X00</td> </tr> </table>	Application Number		Filing Date	October 4, 2000	First Named Inventor	Takeyuki ITABASHI, ET AL.	Examiner Name		Group / Art Unit		Attorney Docket No.	503.39144X00
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TOTAL AMOUNT OF PAYMENT	(\$1,380.00)												

<p><b>METHOD OF PAYMENT (check one)</b></p> <p>1. <input type="checkbox"/> The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:</p> <p>Deposit Account Number: <u>01-2135</u></p> <p>Deposit Account Name: <u>Antonelli, Terry, Stout &amp; Kraus</u></p> <p><input checked="" type="checkbox"/> Charge Any Additional Fee Required Under 37 CFR §§ 1.16 and 1.17</p> <p>2. <input checked="" type="checkbox"/> Payment Enclosed:  <input type="checkbox"/> Check    <input type="checkbox"/> Money Order    <input checked="" type="checkbox"/> Other</p> <p style="text-align: center;"><b>FEE CALCULATION</b></p> <p><b>1. BASIC FILING FEE</b></p> <table style="width: 100%; font-size: small;"> <tr> <th>Large Entity Fee Code (\$)</th> <th>Small Entity Fee Code (\$)</th> <th>Fee Description</th> <th>Fee Paid</th> </tr> <tr> <td>101 690</td> <td>201 345</td> <td>Utility filing fee</td> <td><u>710.00</u></td> </tr> <tr> <td>106 310</td> <td>206 155</td> <td>Design filing fee</td> <td></td> </tr> <tr> <td>107 480</td> <td>207 240</td> <td>Plant filing fee</td> <td></td> </tr> <tr> <td>108 690</td> <td>208 345</td> <td>Reissue filing fee</td> <td></td> </tr> <tr> <td>114 150</td> <td>214 75</td> <td>Provisional filing fee</td> <td></td> </tr> <tr> <td colspan="3" style="text-align: right;"><b>SUBTOTAL (1)</b></td> <td><b>(\$ 710.00)</b></td> </tr> </table> <p><b>2. 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<b>SUBMITTED BY</b>		<b>Complete (if applicable)</b>	
Name (Print/Type)	William I. Solomon	Registration No (Attorney/Agent)	28,565
Signature		Telephone	703-312-6600
		Date	10/04/2000

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ELECTROLESS COPPER PLATING MACHINE THEREOF,  
AND MULTI-LAYER PRINTED WIRING BOARD

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to An electroless  
copper plating method of reducing the concentration of  
byproduct ions and deposition of byproducts in a  
10 plating solution, a device thereof, and an application  
thereof.

2. Description of the Prior Art

A usual electroless copper plating solution  
contains copper ions, a copper ion complexing agent, a  
15 copper ion reducing agent, and a pH conditioner, which  
must be supplied as a plating advances. However, this  
supply increases anions in pairs with copper ions,  
oxidant ions of the copper ion reducing agent, and  
cations of the pH conditioner in the plating solution.

20 These ions increasing in the plating solution will  
deteriorate the physical properties of the plated  
layer, particularly the elongation ratio of the plated  
layer, reducing the reliability of the plated layer.  
Further it reduces the stability of the plating  
25 solution and causes abnormal deposition and autolysis.

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Conventionally, to avoid such problems and keep a constant salt concentration in the plating solution, various plating methods have been taken such as changing plating solutions at short-time intervals, continuously adding a new plating liquid to the plating solution in use. However, these methods require a large quantity of expensive copper plating solution and a lot of labor and money to dispose of liquid wastes.

Japanese Non-examined Patent Publication No.56-136967 (1981) has disclosed a method of continuously removing such cumulative ions by an electro dialysis. This method requires complicated operations to keep the optimum pH for dialysis. Further, the ion selecting membrane which allows plating blocking ions only to penetrate the membrane is mechanically weak, hard to be maintained, and too expensive.

Japanese Non-examined Patent Publication No.7-268638 (1995) has disclosed a plating method characterized by selecting the metallic ion reducing agent and the pH conditioner in the non-electro plating solution so that the oxidant ion of the metallic ion reducing agent and the cation of the pH conditioner may react into an insoluble salt to prevent oxidant ions of said metallic ion reducing

agent from increasing in said plating solution

However, this method is not effective to prevent increase of anions in pairs with metallic ions. The increase of the anions will deteriorate the plating characteristics. This method also discloses that the use of copper oxide or copper hydroxide in copper plating will suppress characteristic deterioration of the plating solution. In this case, however, the solubility of copper oxide or copper hydroxide has a great influence.

Solid copper oxide or copper hydroxide is usually added to the plating solution. If the solid is not dissolved completely into the plating solution, the particles left undissolved are plated as the cores. This causes abnormal deposition or autolysis. Further, copper oxide and copper hydroxide are more expensive than copper sulfate as copper ion sources, which is conventionally used for copper plating. That's the reason why copper oxide and copper hydroxide have not been put in practical use.

Japanese Non-examined Patent Publication No.7-286279 (1995) has disclosed a method of adding barium hydroxide to the non-electro plating solution and removing excessive sulfuric ions as barium sulfate from the plating solution. However, this method using

formalin (35 % aqueous formaldehyde solution) cannot be free from increase of oxidant ions of the copper ion reducing agent in the copper plating solution. The oxidant ions of the copper ion reducing agent in this method are formic ions and cannot be removed because barium formate has too great a solubility to be precipitated.

Further, this method does not blow air into the solution while adding barium hydroxide into the plating solution. When alkaline barium hydroxide is added to the plating solution, the pH value of the plating solution becomes higher. In electroless copper plating, the plating solution becomes unstable when its pH goes too high. Consequently, copper may deposit on unwanted places. This abnormal deposition on printed circuits and the like may cause short-circuits, reducing the yield of products. Deposition on the walls of the plating bath may drastically deteriorate the workability.

The conventional plating equipment is usually designed to directly add copper ions, the copper-ion reducing agent, and the pH conditioner into the plating bath. However, this equipment cannot be free from floating of solid particles of insoluble salt in the plating solution. The floating solid particles

when deposited on wiring boards may cause abnormal deposition on the boards.

If such a solid particle is caught in a through-hole on a printed wiring board, it prevents part of the through-hole from being plated, causing discontinuity of the wiring (which is termed "through-hole void").

In continuous electroless copper plating , byproduct ions such as anions in pairs with copper ions and oxidant ions of the copper ion reducing agent increase in the plating solution. This increasing byproduct ions prevent the electroless copper plating reaction from forming normal plating layers and reduces the quality of the plated layer. This not only reduces the mechanical properties of the plated layer but also causes abnormal deposition of metal on unwanted locations. Up to now, there have been disclosed no effective electroless copper plating method of preventing the increase of plating blocking ions or removing the increased plating blocking ions and refreshing the plating solution.

#### SUMMARY OF THE INVENYION

The main purpose of the present invention is to



provide a method of removing plating blocking ions  
such as anions in pairs with copper ions and oxidant  
ions of the copper ion reducing agent from the  
electroless copper plating solution and keeping a  
constant salt concentration in the electroless copper  
plating solution during plating, a device to realize  
said method, and applications thereof.

The summary of the present invention is as  
follows:

[1] An electroless copper plating method using  
a plating solution containing copper sulfate as copper  
ion sources, and a copper ion complex agent, a copper  
ion reducing agent or glyoxylic acid as a copper ion  
reducing agent, and pH conditioner, wherein said  
method comprises steps of using the hydroxide of an  
alkaline earth metal as said pH conditioner to react  
with sulfuric ions in the electroless copper plating  
solution into a salt of said alkaline earth metal,  
removing the precipitate from the plating solution,  
measuring at least one of the concentration of  
sulfuric ion in the plating solution (when the copper  
ion reducing agent is used) and the concentration of  
oxalic ion in the plating solution (when glyoxylic  
acid is used) and keeping an optimum sulfuric ion or  
oxalic ion concentration or preferentially 0.1 mol per

liter or less of sulfuric ion and 0.2 mol per liter or less of oxalic ion during plating.

[2] An electroless copper plating method using a plating solution containing copper sulfate as copper ion sources, and copper ion complex agent, a copper ion reducing agent or glyoxylic acid as the copper ion reducing agent, and pH conditioner, wherein said method comprises steps of adding at least one of alkaline earth metal, alkaline earth metal oxide, alkaline earth metal hydroxide, and alkaline earth metal salt (excluding sulfuric salt) to the plating solution to react with sulfuric ions in the electroless copper plating solution into a salt of said alkaline earth metal, removing the precipitate from the plating solution, measuring at least one of the concentration of sulfuric ion in the plating solution (when the copper ion reducing agent is used) and the concentration of oxalic ion in the plating solution (when glyoxylic acid is used) and keeping an optimum sulfuric ion or oxalic ion concentration or preferentially 0.1 mol per liter or less of sulfuric ion and 0.2 mol per liter or less of oxalic ion during plating.

[3] An electroless copper plating machine using a plating solution containing copper sulfate as copper

ion sources, and copper ion complex, a copper ion  
reducing agent or glyoxylic acid as a copper ion  
reducing agent, and pH conditioner, wherein said  
device comprises an electroless copper plating bath,  
5 a reaction bath which adds at least one of alkaline  
earth metal, alkaline earth metal hydroxide, alkaline  
earth metal oxide, and alkaline earth metal salt  
(excluding sulfuric salt) to said copper plating  
solution therein to react with and precipitate  
10 sulfuric ions or oxalic ion (when glyoxylic acid is  
used) as an alkaline earth metal salt in said plating  
solution, a filter unit which separates said metallic  
salt precipitate, means for measuring at least one of  
the concentration of sulfuric ion (when the copper ion  
15 reducing agent is used) and the concentration of  
oxalic ion in the plating solution (when glyoxylic  
acid is used), and means for comparing at least one of  
said measured concentrations by a preset reference  
concentration and controlling the quantity of said  
20 alkaline earth metal, alkaline earth metal hydroxide,  
alkaline earth metal oxide, or alkaline earth metal  
salt (excluding sulfuric salt) to be added.

[4] An electroless copper plating machine  
using a plating solution containing metallic ions, an  
25 agent for reducing said metallic ions, and a pH

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conditioner, wherein said machine comprises An  
electroless copper plating bath, a reaction bath  
adding at least a metal or a compound containing a  
metal to said plating solution to precipitate ions  
5 which suppress generation of said plating metal, and a  
ultrafiltration unit.

[5] Said filtration unit is preferably a cross-  
flow type ultrafiltration unit or a filter press type  
ultrafiltration unit.

10 [6] A multi-layer wiring board having insulating  
layers and circuit layers accumulated and cemented  
alternately wherein the circuit layers are  
electrically connected by copper-plated through-holes  
which pass through the insulating layer between said  
15 circuit layers or by copper-plated via-holes whose one  
end is closed and wherein the copper plating of said  
multi-layer wiring board is made by said electroless  
copper plating method.

[7] A module having one or more semiconductor  
20 elements on said multi-layer wiring board.

The method of the present invention removes said  
insoluble salt by saturating it at a temperature lower  
than the plating temperature to cause it to  
precipitate and removing the precipitate. A method of  
25 concentrating the plating solution can also be used to

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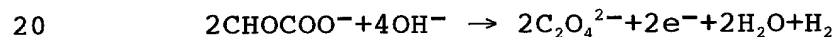
cause the insoluble salt to precipitate.

Removal of said insoluble salt can be done by circulating the plating solution while plating is in progress or in a batch manner when plating is not in progress after sulfuric ions and oxidant ions of the copper ion reducing agent in the non-electro plating solution exceed the preset quantities.

Below will be briefly explained a copper plating using copper sulfate as copper ion sources, as a copper ion source and glyoxylic acid as the copper ion reducing agent.

When copper sulfate as copper ion sources, is used as a copper ion source, the sulfuric ions increase in the plating solution. When glyoxylic acid is used as a copper ion reducing agent, the glyoxylic acid behaves as glyoxalate ions in the plating solution and is reacted into oxalic ions which are the oxidant ions. This reaction is

(Reaction formula 1)



When the concentration of the byproduct ions exceeds a limit (0.1 mol per liter of sulfuric ions or 0.2 mol per liter of oxalic ions), the plating solution will lose its characteristics quickly.

Experimentally, the concentration of the byproduct

ions exceeds the limit when a plating layer of 30 to 60  $\mu\text{m}$  thick is formed under conditions of a plating bath load of 1  $\text{dm}^2$  per liter.

When calcium hydroxide is added as a pH  
5 conditioner, the sulfuric ions in the plating solution are precipitated as calcium sulfate and the concentration of remaining sulfuric ions will become very low (about 0.01 mol per liter or less) as the solubility of calcium sulfate is about 0.15 gram  
10 solute per 100 grams water at 60°C.

Similarly, the oxalic ions in the plating solution are precipitated as calcium oxalate and the concentration of remaining oxalic ions will become extremely low (about  $7 \times 10^{-6}$  mol per liter or less) as  
15 the solubility of calcium oxalate is about 0.001 gram solute per 100 grams water at 60°C. When the plating solution contains sulfuric ions of 0.01 mol per liter or less and the oxalic ions of  $7 \times 10^{-6}$  mol per liter or less, the plating characteristic is excellent and  
20 the plated layer is very ductile.

Under this condition, no abnormal copper deposition is found on non-plating locations and the plating solution is also very stable. To add calcium ions into the plating solution, use a calcium pH  
25 conditioner, calcium powder, calcium acetate, calcium

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carbonate, calcium chloride, calcium oxide, and the like.

The similar result can be obtained when calcium is substituted by barium. When one of the above barium compounds is used, almost all sulfuric ions in the plating solution are precipitated as barium sulfate and the concentration of remaining sulfuric ions will become very low (about  $1.5 \times 10^{-4}$  mol per liter or less) as the solubility of barium sulfate is about 0.0036 gram solute per 100 grams water at 50°C.

Similarly, the oxalic ions in the plating solution are precipitated as barium oxalate and the concentration of remaining oxalic ions will become extremely low (about  $7.9 \times 10^{-5}$  mol per liter or less) as the solubility of barium oxalate is about 0.00175 gram solute per 100 grams water at 60°C.

Air must be blown into the plating solution while said compounds are added into the plating solution to remove the precipitate of sulfuric and oxalic ions. For addition of a substance which shows alkalinity in an aqueous solution and increases the pH value of the plating solution such as calcium hydroxide, barium hydroxide, calcium powder, barium powder, and the like, blowing air into the solution is always required while the substance is added to the plating solution.

A plating method and a plating machine in accordance with the present invention do not limit a complexing agent for the electroless copper plating solution (hereinafter abbreviated as a copper plating solution). In other words, it can be any as far as it can form a stable complex with copper ions such as ethylenediaminetetraacetic acid (EDTA),

Rochelle salt, nitrilotriacetic acid (NTA),

nitrilotripropionic acid (NTP),

ethylenediaminediacetic acid (EDDA),

ethylenediaminepropionicdihydrochloride (EDDP),

iminodiacetic acid (IDA),

trans-1.2-diaminocyclohexane-N,N,N'-tetraacetic acid (CyDTA),

diaminopropanoltetraacetic acid (DPTA-OH),

ethylenediaminediacetic acid (EDDA),

triethylenetetraaminehexaacetic acid (TTHA),

diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA),

dihydroxyethyl glycine (DHEG),

hydroxyethylenediaminetriacetic acid (EDTA-OH),

glycoetherdiaminetetraacetic acid (GEDTA),

nitrilotripropionic acid (NTP),

diaminopropanetetraacetic acid (Methyl-EDTA)

hydroxyethyliminodiacetic acid (HIDA),



ethylenediaminetetraquis (methylenesulfonic acid)  
(EDTPO), etc. As stated above, the sulfuric ions and  
the oxalic ions are precipitated and separated as  
insoluble salts from the plating solution and  
5 consequently the plating solution can keep the optimum  
plating characteristics for a long time. The flow  
sheet of a machine which can offer such effects is  
illustrated in FIG. 1.

The plating bath 1 performs electroless copper  
10 plating (hereinafter abbreviated as copper plating).  
The copper plating solution is circulated along a  
circulation route 2 which passes through a filter  
column 3 (for separating floating objects such as dust  
or solid barium sulfate, barium oxalate, etc.). Part  
15 of the copper plating solution is sent to a reaction  
bath 4 and receives copper ions, copper ion reducing  
agent, and pH conditioner which are lost in plating  
there to recover the optimum concentrations. FIG.1  
shows a heat exchange 13 for heating the plating  
20 solution, a copper sulfate as copper ion sources,  
supply tank 21, a pH conditioner supply tank 21, a  
copper ion reducing agent supply tank 23, and  
circulation pumps 24, 25, and 27.

In the reaction bath, the concentrations of copper  
25 ions, copper ion reducing agent, and pH conditioner to

be added are necessarily higher than the concentrations of those in the plating bath to recover the optimum concentrations of the plating solution in the plating bath with the fed-back copper plating solution. If calcium hydroxide or barium hydroxide is used as a pH conditioner, sulfuric ions and oxalic ions to be removed are precipitated as insoluble salts first in the reaction bath. Further, it sometimes happens that the concentrations of ingredients of the solution in the reaction bath are high enough to make the solution unstable.

In such a case, to prevent the copper plating solution from decomposing, a gas containing oxygen such as the air must be blown into the reaction bath through the gas supply pipe 5. If the solubilities of sulfuric salts and oxalic salts go lower as the liquid temperature falls, it is recommended to cool the copper plating solution in the reaction bath to increase the efficiency of precipitation.

In this case, the copper plating solution passing through a pre-cooling heat exchange 6 can be supplied to the reaction bath or the reaction bath itself can be cooled. As it is desirable to heat the cooled copper plating solution to a desired solution temperature before feeding it back to the plating bath,

the copper plating solution coming from the reaction bath is fed back to the plating bath through a heating heat exchange 7.

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5 A concentration analyzer 8 measures the concentration of copper ions, the concentration of the reducing agent, and the pH of the plating solution in the reaction tank. The quantities of ingredients to be supplied are controlled by pumps 9, 10, and 11 so that the measured concentrations may be the predetermined  
10 concentrations. The concentrations of sulfuric ions and oxalic ions can be measured by chromatography. Part of the plating solution is taken out from the reaction bath for measurement. Besides chromatography, the measurement can be done by a capillary  
15 electrophoresis analyzer.

The copper plating solution supplied with copper ions, copper ion reducing agent, and pH conditioner from the reaction bath is fed to a ultra filtration unit 12. The ultra filtration unit 12 contains an  
20 ultra filtration membrane which separates the inner copper plating solution coming from the reaction bath from the outer copper plating solution coming from the plating bath. This is a cross-flow type ultra filtration unit. FIG.2 is a diagrammatic illustration  
25 of the ultra filtration unit explaining the principle

thereof. FIG.2 shows fine particles crystals 29, a cross-flow type ultra filtration unit 12, an ultra filtration membrane 31, a flow of plating solution 32, and a filtrate 33.

5        Using the characteristics of the ultra filtration unit that lets ions and low molecular organic compounds penetrate the membrane but blocks fine particles, the solid precipitate produced in the reaction bath are separated and removed out from the  
10       system. In other words, only ions passing through the ultra filtration membrane can be fed back to the plating bath and solid components can be continuously removed from the system.

15       In the cross-flow filtration, the copper plating solution flows along the surface of the membrane. This prevents the membrane from being blocked quickly. Only the filtrate which passes through the membrane is fed back to the plating bath. This prevents the  
20       crystallized fine particles from returning to the plating solution. The pore size of the membrane is 0.5 microns or less preferentially 0.1 microns or less.

25       The filtration of the present invention can be any as far as sulfuric and oxalic salts produced in the reaction bath are not fed back to the plating bath. Preferable filtration methods are a filter pressing

method, a cross-flow method, etc.

This method enables a long stable electroless copper plating (hereinafter abbreviated as copper plating) with sulfuric and oxalic ion concentrations low in the copper plating solution.

The purpose of the present invention can be realized with the use of a similar method and device in accordance with the present invention even when a compound which will not produce any insoluble salt such as potassium hydroxide, etc. is used as a pH conditioner, when calcium or barium is added singly in the reaction bath or when calcium or barium carbonate, acetate, oxide, or chloride is added to the copper plating solution.

However, when calcium carbonate and/or barium carbonate are used, carbonic ions increase in the copper plating solution. When calcium acetate and/or barium acetate are used, acetic ions increase in the copper plating solution. Similarly, when calcium chloride and/or barium chloride are used, chloric ions increase in the copper plating solution.

Therefore, for the use of a calcium salt and/or a barium salt, the quantity of the salt should be such that its salt precipitate may not give any influence upon the plating characteristics. It is required to

estimate the influence of the salt in advance.

Contrarily, calcium hydroxide, barium hydroxide, calcium, barium, calcium oxide, and barium oxide (when added to the copper plating solution) will not increase ions in the copper plating solution and are preferable as they can make the plating characteristics stable for a long time period.

Potassium hydroxide can be used as a pH conditioner even when calcium hydroxide and or barium hydroxide are used to produce oxalic or sulfuric salt precipitate. Also in this case, the purpose of the present invention can be realized.

In the above explanation, if the solubility of a compound (e.g. calcium hydroxide) to be added is low, a slurry of the compound is sometimes preferable to an aqueous solution of the compound. In this case, a slurry pump is usually used to feed the slurry compound to the reaction bath.

According to the present invention, byproduct ions which increase as a non-electro plating reaction advances can be eliminated and consequentially the electroless copper plating solution can have a longer working life, drastically reducing the plating cost.

BRIEF DESCRIPTION OF DRAWINGS

FIG.1 is a flow diagram explaining the configuration of a plating machine in accordance with the present invention.

5        FIG.2 is a schematic diagram of the ultra filtration unit used in the plating machine in accordance with the present invention.

10        FIG.3 is a flow diagram explaining the configuration of a plating machine which is a preferred embodiment of the present invention.

FIG.4 is a flow diagram explaining the configuration of a plating machine which is another preferred embodiment of the present invention.

15        FIG.5 is a flow diagram explaining the configuration of a plating machine which is another preferred embodiment of the present invention.

20        FIG.6 is a schematic sectional diagram of a module having semiconductor elements on a multi-layer board plated in accordance with the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

### [Embodiment 1]

25        A first embodiment of the present invention uses copper sulfate as copper ion sources, as a copper ion

source, glyoxylic acid as a copper ion reducing agent and barium hydroxide as a pH conditioner. This embodiment uses EDTA pentasodium as a complexing agent because the solubility of barium hydroxide is not so great.

Below are listed the ingredients of the plating solution and the plating condition.

(Ingredients)

- Copper (II) sulfate pentahydrate 0.04 mol per liter
- EDTA pentasodium 0.1 mol per liter
- Glyoxylic acid 0.03 mol per liter
- Barium hydroxide 0.01 mol per liter
- 2,2' bipyridyl 0.0002 mol per liter
- Polyethylene glycol (mean molecular weight = 600) 0.03 mol per liter

The concentration of barium hydroxide is controlled to keep the pH of the plating solution at 12.3.

(Plating condition)

- pH 12.3
- plating solution temperature 70°C

A copper wiring pattern was plated on a test board in said copper plating solution. The stability of the plating solution and the quality of the plated layer



were evaluated from the existence of abnormal deposition of copper. The test board was prepared as stated below. The physical property of the plated layer was also evaluated.

5 (Preparation of a test board)

A test board was prepared by coating both surfaces of a 0.6mm-thick glass-sheet reinforced resin laminated board with an adhesive containing acrylonitrilebutadiene rubber modified phenol resin as the main ingredient, and hardening thereof at 160°C for ten minutes. The hardened test board has an adhesive layer of about 30 microns thick on each surface. Then, the test board was drilled at preset locations and dipped in a coarsening liquid containing chromic anhydride and hydrochloric acid to coarsen the adhesive surfaces.

Next, the board was dipped for ten minutes in a single-liquid palladium colloidal catalyst solution (fabricated by Hitachi Kasei Co., Ltd. acid aqueous solution containing intensifier HS101B) as a copper plating catalyst, washed clean with water, and dried up at 120°C for 20 minutes.

Both surfaces of the board were coated with a dry-film photo-resist layer of 35 microns thick (SR-3000 fabricated by Hitachi Kasei Co., Ltd). A mask of a

test pattern comprising lines of 60 microns thick was placed on the photo resist surface of the board. The board was exposed to light and developed. As the result, the non-pattern parts on the surface of the board are all covered with the photo-resist.

The test board prepared above and a stainless steel plate were both dipped in the plating solution at a liquid temperature of 70°C and plated with a load of 1 dm<sup>2</sup> per liter.

The stainless steel plate was prepared by dipping the plate in 17% hydrochloric aqueous solution for 2 minutes, dipping it in the above palladium collidal solution for 10 minutes, and washing it thoroughly. While plating is in progress, air was blown into the plating solution to stir up the solution. A prepared liquid (listed below) was supplied to the plating solution to make the concentration of copper ions, the concentration of glyoxylic acid (copper ion reducing agent), and the pH constant.

(1) Copper ion supplement ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) 200 grams  
Water Quantity required to make one liter of the solution

(2) Glyoxylic acid (copper ion reducing agent)  
supplement 40% glyoxylic acid solution

(3) pH conditioner ( $\text{Ba}(\text{OH})_2$ ) 40 grams

Water Quantity required to make one liter of the solution

One plating cycle comprises a plating step to form a 30 $\mu$ m-thick copper layer on the stainless steel plate and the pattern area of the test board. At the end of each plating cycle, the plated copper layer was peeled off from the stainless steel plate, cut into a piece of 1.25 cm by 10 cm. The mechanical strength of the piece was measured by an ordinary tensile tester.

The precipitates (barium sulfate, barium oxalate, and others) which were formed during plating were filtered and removed by circulation and filtration of the plating solution. After each plating cycle is completed, the plating solution is cooled down to the room temperature (25°C) and filtered to remove the precipitates (barium sulfate, barium oxalate, and others) before the succeeding plating cycle. The concentrations of the sulfuric and oxalic ions in this clean plating solution were measured by chromatography. Table 1 shows the result of the measurement.

Table 1

		Unit	Number of plating cycles						
			1	2	3	4	5	6	7
5	Embodiment 1	Conc. of sulfuric ions	mol/l	$8 \times 10^{-3}$	$9 \times 10^{-3}$	$9 \times 10^{-3}$	$8 \times 10^{-3}$	$8 \times 10^{-3}$	$8 \times 10^{-3}$
		Conc. of oxalic ions	mol/l	$7 \times 10^{-6}$	$7 \times 10^{-6}$	$7 \times 10^{-6}$	$6 \times 10^{-6}$	$7 \times 10^{-6}$	$6 \times 10^{-6}$
		Ductility of plate film	%	9.8	10.5	9.7	10.1	7.8	10.3
		Abnormal deposition	-	None	None	None	None	None	None
10	Embodiment 2	Conc. of sulfuric ions	mol/l	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$
		Conc. of oxalic ions	mol/l	$7 \times 10^{-5}$	$7 \times 10^{-5}$	$6 \times 10^{-5}$	$7 \times 10^{-5}$	$6 \times 10^{-5}$	$5 \times 10^{-5}$
		Ductility of plate film	%	10.1	8.5	9.6	7.1	6.8	10.2
		Abnormal deposition	-	None	None	None	None	None	None
15	Embodiment 3	Conc. of sulfuric ions	mol/l	$9 \times 10^{-3}$	$9 \times 10^{-3}$	$8 \times 10^{-3}$	$8 \times 10^{-3}$	$9 \times 10^{-3}$	$8 \times 10^{-3}$
		Conc. of formic ions	mol/l	0.12	0.28	0.42	0.62	0.78	0.92
		Ductility of plate film	%	10.5	8.8	7.5	6.8	5.2	4.6
		Abnormal deposition	-	None	None	None	None	None	Little
20	Embodiment 4	Conc. of sulfuric ions	mol/l	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$	$1 \times 10^{-4}$
		Conc. of formic ions	mol/l	0.11	0.26	0.43	0.62	0.77	0.95
		Ductility of plate film	%	11.0	10.2	7.6	7.3	5.5	4.3
		Abnormal deposition	-	None	None	None	None	None	Little
25	Embodiment 6	Conc. of sulfuric ions	mol/l	$9 \times 10^{-3}$	$9 \times 10^{-3}$	$9 \times 10^{-3}$	$8 \times 10^{-3}$	$8 \times 10^{-3}$	$8 \times 10^{-3}$
		Conc. of oxalic ions	mol/l	$7 \times 10^{-6}$	$7 \times 10^{-6}$	$7 \times 10^{-6}$	$7 \times 10^{-6}$	$7 \times 10^{-6}$	$7 \times 10^{-6}$
		Ductility of plate film	%	10.2	8.7	9.6	8.8	8.5	9.8
		Abnormal deposition	-	None	None	None	None	None	None
	Comparative embodiment 1	Conc. of sulfuric ions	mol/l	0.08	0.12	0.19	0.35	0.55	-
		Conc. of formic ions	mol/l	0.12	0.24	0.38	0.67	0.98	-
		Ductility of plate film	%	9.8	7.5	5.4	3.2	1.2	-
		Abnormal deposition	-	None	Little	Some	Some	Deposition	-
	Comparative embodiment 2	Conc. of sulfuric ions	mol/l	0.08	0.13	0.18	0.33	0.56	-
		Conc. of oxalic ions	mol/l	0.12	0.24	0.37	0.77	1.02	-
		Ductility of plate film	%	9.7	7.7	5.2	2.8	1.0	-
		Abnormal deposition	-	None	Little	Some	Some	Deposition	-

The concentrations of sulfuric and oxalic ions in the plating solution were measured after the plating solution was filtered at the end of each plating cycle.

5 Even after seven plating cycles, the sulfuric ion concentration was  $1.5 \times 10^{-4}$  mol per liter or less and the oxalic ion concentration was  $7.9 \times 10^{-5}$  mol per liter or less. The ductility of the obtained plated layer was 6% or more and was not deteriorated so much  
10 as the number of plating cycles increased. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles were made.

15 As stated above, the method in accordance with the present invention is found to suppress increase of sulfuric and oxalic ions in the plating solution. This is due to the use of barium hydroxide as a pH conditioner which causes the sulfuric and oxalic ions  
20 to precipitate as insoluble barium salts. This precipitate is separated from the plating solution and the plating solution can be almost free from sulfuric and oxalic ions.

25 The long excellent plating characteristics can be obtained by plating under conditions of the sulfuric

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ion concentration of 0.1 mol per liter or less and the oxalic ion concentration of 0.2 mol per liter or less in the plating solution.

[Embodiment 2]

5       A second embodiment of the present invention was done under the same conditions as the first embodiment but barium hydroxide as a pH conditioner was substituted by calcium hydroxide. As the solubility of calcium hydroxide is very low (approx. 1.7 gram solute  
10       per 1 liter water), its aqueous solution is not available. Therefore calcium hydroxide in slurry (obtained by powering calcium hydroxide and adding pure water thereto) was used.

15       Powdered calcium hydroxide has greater surfaces in contact with the plating solution and can easily react with sulfuric and oxalic ions into insoluble precipitates in the plating solution although the solubility of calcium hydroxide is very low. In this case, however, the efficiency of removal of sulfuric  
20       and oxalic ions from the plating solution is dependent upon the granule sizes of the calcium hydroxide powder, the rate of solution stirring, and so on. They must be optimized in advance.

25       To prevent a lot of crystals including undissolved calcium hydroxide from existing in the

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plating solution, this embodiment employs a method of adding a slurry of calcium hydroxide into the reaction bath which is provided separately from the plating bath instead of adding a slurry of calcium hydroxide directly into the plating bath, mixing the slurry and the plating solution in the plating bath, removing the precipitate by the ultra filtration unit, and feeding back the filtered plating solution to the plating bath.

Table 1 shows the result of evaluation of plating characteristics. This method can keep the sulfuric and oxalic concentrations very low (0.01 mol per liter or less of sulfuric ion and  $7 \times 10^{-6}$  mol per liter or less of oxalic ion) even after seven plating cycles.

The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles were made.

[Embodiment 3]

A third embodiment of the present invention uses copper sulfate as copper ion sources, as a copper ion source, formaldehyde as a copper ion reducing agent and barium hydroxide as a pH conditioner. In this case,

the oxidant ion of the formaldehyde is formic acid.  
This embodiment assumes that formic acid cannot be  
removed as a precipitate. Below are listed the  
ingredients of the plating solution and the plating  
condition.

(Ingredients)

- Copper (II) sulfate pentahydrate 0.04 mol per liter
- EDTA pentasodium 0.1 mol per liter
- Formaldehyde 0.03 mol per liter
- Barium hydroxide 0.01 mol per liter
- 2,2' bipyridyl 0.0002 mol per liter
- Polyethylene glycol  
(mean molecular weight = 600) 0.03 mol per liter

The concentration of barium hydroxide is  
controlled to keep the pH of the plating solution at  
12.3.

(Plating condition)

- pH 12.3
- Liquid temperature 70°C

This embodiment plated the same test board in the  
same method as Embodiment 1 in the above copper  
plating solution. The physical property of the  
obtained plated layer (foil), abnormal deposition, and  
concentrations of salts in the plating solution were



tested and measured in the same manner as Embodiment 1.  
37% formaldehyde aqueous solution is used to supply  
the copper ion reducing agent.

Table 1 shows the result of evaluation of plating  
characteristics. The concentration of sulfuric ions in  
the plating solution was measured after the plating  
solution was filtered at the end of each plating cycle.

This method can keep the sulfuric concentration  
very low ( $1.5 \times 10^{-4}$  mol per liter or less) even after  
seven plating cycles.

The ductility of the plated layer (foil) formed in  
the seventh plating cycle was under half as much as  
that of the plated layer (foil) formed in the first  
plating cycle, but it was strong enough to assure the  
reliability. Further, within five plating cycles, no  
abnormal deposition was visually detected on the test  
board, in the plating bath, pipings, and so on. The  
plating solution was extremely steady. After sixth and  
seventh plating cycles, a little abnormal deposition  
was found on the test board and in the plating bath  
but it was not much enough to cause short-circuiting  
of a wiring pattern on the test board.

#### [Embodiment 4]

A fourth embodiment of the present invention was  
done under the same conditions as the third embodiment

but the pH conditioner for the plating solution and the supplement is calcium hydroxide. As the solubility of calcium hydroxide is very low, its aqueous solution is not available. Therefore calcium hydroxide in slurry) was used as in the second embodiment

The result of measurement is listed in Table 1. This method can keep the sulfuric concentration very low (0.01 mol per liter or less) after the seven plating cycles. The ductility of the plated layer (foil) formed in the seventh plating cycle was under half as much as that of the plated layer (foil) formed in the first plating cycle, but it was strong enough to assure the reliability.

Further, within five plating cycles, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady. After sixth and seventh plating cycles, a little abnormal deposition was found on the test board and in the plating bath but it was not much enough to cause short-circuiting of a wiring pattern on the test board.

[Embodiment 5]

A copper plating solution of a fifth embodiment of the present invention was prepared using copper sulfate as copper ion sources, as a copper ion source,

glyoxylic acid as a copper ion reducing agent and potassium hydroxide as a pH conditioner in preparation of a plating solution.

(Ingredients)

- 5        - Copper (II) sulfate pentahydrate                      0.04 mol per liter
- EDTA pentasodium                                      0.1 mol per liter
- Glyoxylic acid    0.03 mol per liter
- Potassium hydroxide                                    0.03 mol per liter
- 10       - 2,2' bipyridyl    0.0002 mol per liter
- Polyethylene glycol
- (mean molecular weight = 600) 0.03 mol per liter

The concentration of potassium hydroxide is controlled to keep the pH of the plating solution at

15       12.3.

(Plating condition)

- pH    12.3
- Liquid temperature                                        70°C

A prepared liquid (listed below) was supplied to

20       the plating solution to make the concentration of copper ions, the concentration of glyoxylic acid (a copper ion reducing agent), and the pH constant although they decrease as a plating advances.

- (1) Copper ion supplement ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ )    200 grams
- 25                      Water    Quantity required to make one liter of

the solution

(2) Glyoxylic acid (copper ion reducing agent)  
supplement 40% glyoxylic acid solution

(3) pH conditioner ( $\text{Ba}(\text{OH})_2$ ) 40 grams

5 Water Quantity required to make one liter of  
the solution

As seen from the above, aqueous solution of barium  
hydroxide is used to keep the pH of the plating  
solution constant although potassium hydroxide is used  
10 as a pH conditioner when the plating solution is  
prepared.

Even after seven plating cycles, the sulfuric ion  
concentration was  $1.5 \times 10^{-4}$  mol per liter or less and  
the oxalic ion concentration was  $7.9 \times 10^{-5}$  mol per  
15 liter or less. The ductility of the obtained plated  
layer was 6% or more and was not deteriorated so much  
as the number of plating cycles increased. Further, no  
abnormal deposition was visually detected on the test  
board, in the plating bath, pipings, and so on. The  
20 plating solution was extremely steady even after seven  
plating cycles were made.

[Embodiment 6]

A sixth embodiment of the present invention uses a  
plating solution containing copper sulfate as copper  
25 ion sources, as a copper ion source, glyoxylic acid

as a copper ion reducing agent and potassium hydroxide as a pH conditioner. Below are listed the ingredients of the plating solution and the plating condition.

(Ingredients)

- 5        - Copper (II) sulfate pentahydrate                      0.04 mol per liter
- EDTA pentasodium                                      0.1 mol per liter
- Glyoxylic acid    0.03 mol per liter
- Potassium hydroxide                                    0.03 mol per liter
- 10       - 2,2' bipyridyl    0.0002 mol per liter
- Polyethylene glycol
- (mean molecular weight = 600) 0.03 mol per liter

The concentration of potassium hydroxide is controlled to keep the pH of the plating solution at

15       12.3.

(Plating condition)

- pH    12.3
- Liquid temperature                                        70°C

This embodiment plated according to processing flow illustrated in FIG.1 using the above plating solution. In other words, the copper plating was made in the plating bath 1. The plating solution is circulated through a filtration column 3 along the circulation path 2.

25       Part of the copper plating solution is sent to a

reaction bath 4 and receives copper ions, copper ion reducing agent, and pH conditioner to supplement the lost quantities of ingredients. The composition of the supplemental solution is listed below.

- 5           (1) Copper ion supplement ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ )   200  
grams

Water Quantity required to make one liter of  
the solution

- 10           (2) Glyoxylic acid (copper ion reducing agent)  
supplement   40% glyoxylic acid solution

- (3) pH conditioner (KOH)   200 grams

Water Quantity required to make one liter of  
the solution

15           Calcium powder was added to the plating solution  
in the reaction bath to react with sulfuric and oxalic  
ions into insoluble salts. As the pH of the plating  
solution increases when the calcium powder is added,  
the pH conditioner is added to the plating solution to  
decrease the pH. Further, the calcium powder generates  
20   heat of dissolution when it dissolves into the plating  
solution. You must take a very care when dissolving  
the powder.

Therefore, the reaction bath was cooled for  
efficient separation of the precipitate of oxalic salt.

25           When the calcium powder is added, the plating

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solution has lots of precipitates (calcium sulfate, calcium oxalate, and calcium particles which remain un-dissolved). Embodiment 6 removed these precipitates from the plating solution by the ultra filtration unit, regulated the concentration of copper ions, the concentration of glyoxylic acid and the pH to predetermined values, then fed back the plating solution to the plating bath 1.

Table 1 shows the result of evaluation of plating characteristics (the concentration of sulfuric ions, the concentration of oxalic ions, the ductility of the plated layer, and detection of abnormal deposition) of each plating cycle.

The concentration of sulfuric ions and the concentration of oxalic ions in the table are the result of measurement after each plating cycle is completed. This embodiment can keep the sulfuric and oxalic concentrations very low (0.01 mol per liter or less of sulfuric ion and  $7 \times 10^{-6}$  mol per liter or less of oxalic ion) even after seven plating cycles.

The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating

solution was extremely steady even after seven plating cycles were made.

[Embodiment 7]

A seventh embodiment of the present invention was done under the same conditions as Embodiment 6 but calcium powder is substituted by barium oxide to react with sulfuric and oxalic ions into precipitates. The testing method of this embodiment is the same as Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low ( $1.5 \times 10^{-4}$  mol per liter or less of sulfuric ion and  $7.9 \times 10^{-5}$  mol per liter or less of oxalic ion) even after seven plating cycles. The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles were made.

[Embodiment 8]

An eighth embodiment of the present invention was done under the same conditions as Embodiment 6 but calcium powder is substituted by barium carbonate to react with sulfuric and oxalic ions into precipitates.



The testing method of this embodiment is the same as Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low ( $1.5 \times 10^{-4}$  mol per liter or less of sulfuric ion and  $7.9 \times 10^{-5}$  mol per liter or less of oxalic ion) even after seven plating cycles. The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles.

However, it was found the plating rate reduced as the carbonate increased in the plating solution. As the result of visual checks, the plating solution was extremely steady even after seven plating cycles were made, but a little abnormal deposition was found on the test board.

As stated above, the most excellent barium compound to be added to the plating solution to react with sulfuric and oxalic ions into precipitates is barium oxide, barium hydroxide, or simple substance of barium as they will not increase ions in the plating solution.

Although barium carbonate added to the plating solution as in this embodiment can suppress increase of sulfuric and oxalic ions in the plating solution, increase of carbonate ions was recognized. However,

the plating characteristic of this embodiment is better than that of a method which does not use this embodiment. By plating with the concentration of sulfuric ions 0.1 mol per liter and the concentration of oxalic ions 0.2 mol per liter in the plating solution, the excellent plating characteristic can be kept for a long time. This is the effect of this embodiment.

[Embodiment 9]

A ninth embodiment of the present invention was done under the same conditions as Embodiment 6 but calcium powder is substituted by barium acetate to react with sulfuric and oxalic ions into precipitates. The testing method of this embodiment is the same as Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low ( $1.5 \times 10^{-4}$  mol per liter or less of sulfuric ion and  $7.9 \times 10^{-5}$  mol per liter or less of oxalic ion) even after seven plating cycles.

The ductility of the obtained copper layer (foil) was 3% or more and a little inferior to that of the embodiment using barium hydroxide. As the result of visual checks, the plating solution was extremely steady even after seven plating cycles were made, but a little abnormal deposition was found on the test

board. It is assumed that this is caused by the increase of acetic ions in the plating solution assumed

Although barium acetate added to the plating solution as in this embodiment can suppress increase of sulfuric and oxalic ions in the plating solution, increase of acetate ions was recognized. However, the plating characteristic of this embodiment is better than that of a method which does not use this embodiment. By plating with the concentration of sulfuric ions 0.1 mol per liter and the concentration of oxalic ions 0.2 mol per liter in the plating solution, the excellent plating characteristic can be kept for a long time.

[Embodiment 10]

A tenth embodiment of the present invention was done under the same conditions as Embodiment 6 but calcium powder is substituted by barium chloride to react with sulfuric and oxalic ions into precipitates. The testing method of this embodiment is the same as Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low ( $1.5 \times 10^{-4}$  mol per liter or less of sulfuric ion and  $7.9 \times 10^{-5}$  mol per liter or less of oxalic ion) even after seven plating cycles.

The ductility of the obtained copper layer (foil) was 3% or more and a little inferior to that of the embodiment using barium hydroxide. As the result of visual checks, the plating solution was extremely steady even after seven plating cycles were made, but a little abnormal deposition was found on the test board. It is assumed that this is caused by the increase of chloric ions in the plating solution assumed

As stated above, the most excellent barium compound to be added to the plating solution to react with sulfuric and oxalic ions into precipitates is barium hydroxide, barium oxide, or simple substance of barium as they will not increase ions in the plating solution.

Although barium chloride added to the plating solution as in this embodiment can suppress increase of sulfuric and oxalic ions in the plating solution, increase of chloride ions was recognized. However, the plating characteristic of this embodiment is better than that of a method which does not use this embodiment. By plating with the concentration of sulfuric ions 0.1 mol per liter and the concentration of oxalic ions 0.2 mol per liter in the plating solution, the excellent plating characteristic can be

kept for a long time. This is the effect of this embodiment.

[Embodiment 11]

5 This embodiment of the present invention was done under the same conditions as Embodiment 6 but calcium to be added to the plating solution is substituted by barium to react with sulfuric and oxalic ions into precipitates.

10 This embodiment can keep the sulfuric and oxalic concentrations very low ( $1.5 \times 10^{-4}$  mol per liter or less of sulfuric ion and  $7.9 \times 10^{-5}$  mol per liter or less of oxalic ion) even after seven plating cycles. The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after  
15 many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles were made.

20 [Embodiment 12]

A twelfth embodiment of the present invention uses copper sulfate as copper ion sources, as a copper ion source, formaldehyde as a copper ion reducing agent and potassium hydroxide as a pH conditioner. In this  
25 case, the oxidant ion of the formaldehyde is formic

acid. This embodiment assumes that formic acid cannot be removed as a precipitate. Below are listed the ingredients of the plating solution and the plating condition.

5 (Ingredients)

- Copper (II) sulfate pentahydrate

0.04 mol per liter

- EDTA pentasodium 0.1 mol per liter

- Formaldehyde 0.03 mol per liter

10 - Potassium hydroxide 0.03 mol per liter

- 2,2' bipyridyl 0.0002 mol per liter

- Polyethylene glycol

(mean molecular weight = 600) 0.03 mol per liter

The concentration of potassium hydroxide is  
15 controlled to keep the pH of the plating solution at  
12.3.

(Plating condition)

- pH 12.3

- Liquid temperature 70°C

20 This embodiment plated the same test board in the  
same method as Embodiment 1 in the above copper  
plating solution in a plating flow illustrated in FIG.1.

The copper plating solution is circulated along a  
circulation route 2 which passes through a filter  
25 column 3.

Part of the copper plating solution is sent to a reaction bath 4 and receives copper ions, copper ion reducing agent, and pH conditioner which are lost in plating there to recover the optimum concentrations.

5 The composition of the supplemental solution is listed below.

(1) Copper ion supplement ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) 200 grams

10 Water Quantity required to make one liter of the solution

(2) Formaldehyde (copper ion reducing agent) supplement 37% glyoxylic acid solution

(3) pH conditioner (KOH) 200 grams

15 Water Quantity required to make one liter of the solution

Calcium powder was added to the plating solution in the reaction bath to react with sulfuric ions into insoluble salt. As the pH of the plating solution increases when the calcium powder is added, the pH conditioner was added to the plating solution to decrease the pH. Further, the calcium powder generates a lot of heat of dissolution when it dissolves into the plating solution. You must take a very care when dissolving the powder. Therefore, the reaction bath was cooled for efficient separation of the precipitate

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of oxalic salt.

When the calcium powder is added, the plating solution has lots of precipitates (calcium sulfate and calcium particles which remain un-dissolved). This embodiment removed these precipitates from the plating solution by the ultra filtration unit, regulated the concentration of copper ions, the concentration of formaldehyde and the pH to predetermined values, then fed back the plating solution to the plating bath 1.

This embodiment can keep the sulfuric concentration very low ( $1.5 \times 10^{-4}$  mol per liter or less) even after seven plating cycles. The ductility of the plated layer (foil) formed in the seventh plating cycle was 3% which is under half as much as that of the plated layer (foil) formed in the first plating cycle, but it was strong enough to assure the reliability.

Further, within five plating cycles, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady. After sixth and seventh plating cycles, a little abnormal deposition was found on the test board and in the plating bath but it was not much enough to cause short-circuiting of a wiring pattern on the test board.



[Comparative embodiment 1]

This embodiment performed copper plating using a conventional copper plating solution which contained formaldehyde as a copper ion reducing agent and sodium hydroxide as a pH conditioner.

The pH and the temperature of the plating solution were respectively 12.5 and 70°C. In this case, the oxidant ion of the formaldehyde is formic acid and the solubility of sodium formate is extremely high (99.6 grams solute per 100 grams water at 25°C). Further, the solubility of sodium sulfate is also high (21.9 grams solute per 100 grams water at 25°C). Therefore, sodium formate and sodium sulfate will never precipitate even after the copper plating solution is cooled and these ions (byproduct ions) cannot be removed.

The concentration of sulfuric ions, the concentration of formic ions, and the physical quantity of the plated layer (foil) in repetitive plating are illustrated in Table 1.

Table 1 shows that, as the repetitive plating advances, the sulfuric and formic ions increase in the plating solution and the ductility of the plated layer (foil) decreases. Further, the copper plating solution became unstable as the plating advanced. The plating

solution started autolysis.halfway in the fifth  
plating and was disabled to plate.

[Comparative embodiment 2]

5 This embodiment performed copper plating using the  
same copper plating solution as Comparative Embodiment  
2 but calcium hydroxide as the pH conditioner was  
substituted by potassium hydroxide. The pH and the  
temperature of the plating solution were respectively  
12.5 and 70°C.

10 In this case, the solubility of potassium sulfate  
is high (10.8 grams solute per 100 grams water at 25°C).  
Therefore, sodium sulfate will never precipitate and  
the sulfuric ions cannot be removed.

15 Similarly, the solubility of potassium oxalate is  
also high (35.9 grams solute per 100 grams water at  
25°C). Therefore, potassium oxalate did not  
precipitate even after the copper plating solution was  
cooled and the oxalic ions could not be removed.

20 The concentration of sulfuric ions, the  
concentration of oxalic ions, and the physical  
quantity of the plated layer (foil) in repetitive  
plating are illustrated in Table 1.

25 Table 1 shows that, as the repetitive plating  
advances, the sulfuric and oxalic ions increases in  
the plating solution and the ductility of the plated

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layer (foil) decreases. Further, the copper plating solution became unstable as the plating advanced. The plating solution started autolysis halfway in the fifth plating and was disabled to plate.

5       As seen from the above, it is apparatus that methods which are not in accordance with the present invention cause blocking ions to increase in the plating solution and the resulting plating characteristics are deteriorated. This has proven that  
10       the present invention has the advantage.

[Embodiment 13]

Below will be explained a plating machine which is one of the embodiment in accordance with the present invention. FIG.3 is a flow diagram showing the  
15       configuration of a plating machine in accordance with the present invention.

The copper plating was made in the plating bath 1. The copper plating solution is circulated through a filtration column 3 along a circulation path 2 to  
20       remove solids floating in the copper plating solution. The device has another circulation path passing through a heat exchange 13 to heat up the copper plating solution to a predetermined temperature.

Part of the copper plating solution is sent to a  
25       reaction bath 4 and receives copper ions, copper ion

reducing agent, and pH conditioner to supplement the lost quantities of ingredients.

In the reaction bath 4, the concentrations of copper ions, copper ion reducing agent, and pH conditioner to be added are necessarily higher than the concentrations of those in the plating bath to recover the optimum concentrations of the plating solution in the plating bath 1 with the fed-back copper plating solution.

To prevent the copper plating solution from decomposing in the reaction bath 4, a gas containing oxygen gas such as the air is blown into the copper plating solution in the reaction bath through a gas supply valve 5 to stir up the solution with the gas. A concentration analyzer 8 measures the concentration of copper ions, the concentration of the reducing agent, and the pH of the plating solution in the reaction tank. The quantities of ingredients to be supplied are controlled by pumps 9, 10, and 11 so that the measured concentrations may be the predetermined concentrations.

Pumps 9, 10, and 11 respectively supply copper sulfate as copper ion sources, aqueous solution, glyoxylic acid aqueous solution, and barium hydroxide aqueous solution in that order.

The concentrations of copper ions, the copper ion

reducing agent, and the pH conditioner of the copper  
plating solution in the reaction bath are higher than  
those of the plating solution in the plating bath.  
Barium sulfate and barium oxalate are saturated and  
precipitated first in the reaction bath 4 as the  
copper plating solution is cooled by the heat exchange  
6 before entering the reaction bath 4.

These precipitates (fine crystallized particles)  
are separated from the copper plating solution by the  
cross-flow type ultra filtration unit 12. The filtered  
clean copper plating solution is fed back to the  
plating bath through the heating heat exchange 7.

The copper plating solution containing a lot of  
precipitate is sent to the settling bath 14 in the  
upstream side of the reaction bath 4. Only the  
supernatant plating solution overflows a weir which is  
provided between the settling bath 14 and the reaction  
bath 4 back into the reaction bath 4.

70% or more of the solid precipitate in the copper  
plating solution sent to the settling bath 14 remains  
settled and is taken out of the system.

As stated above, the device in accordance with the  
present invention can remove sulfuric and oxalic ions  
which deteriorate the plating characteristics as  
barium salts and keep an excellent plating

characteristic for a long time.

[Embodiment 14]

FIG.4 is a flow diagram of a plating machine using a filter press type ultra filtration unit. This  
5 embodiment uses almost the same units as those of Embodiment 13 and performs the similar operations. The explanation is omitted here. Unit 17 is a recovery tank.

10 This embodiment is characterized in that the whole reaction bath 4 is cooled further by water sent from the cooling unit 15 after part of the copper plating solution is supplied to the reaction bath 4.

15 The concentrations of copper ions, the copper ion reducing agent, and the pH conditioner of the copper plating solution in the reaction bath 4 are higher than those of the plating solution in the plating bath 1 and the reaction bath 4 is cooled by water from the cooling unit 15. Therefore, barium sulfate and barium oxalate are first saturated and easily precipitated in  
20 the reaction bath.

These precipitates (fine crystallized particles) are separated from the copper plating solution by the filter press type ultra filtration unit 16. The filtered clean copper plating solution is fed back to  
25 the plating bath 1 through the heating heat exchange 7.

5           As stated above, the device in accordance with the present invention can remove sulfuric and oxalic ions which deteriorate the plating characteristics as barium salts and keep an excellent plating characteristic for a long time.

## 10

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ions are regulated by a pump 9 for supplying copper sulfate as copper ion sources, aqueous solution, a pump 10 for supplying glyoxylic acid aqueous solution, and an analyzing unit 8.

5       The quantity of sulfuric ions in the copper plating solution can be calculated from the quantity of copper sulfate as copper ion sources, solution supplied by pump 9. The quantity of oxalic ions in the copper plating solution is calculated as the  
10       difference between the quantity of oxalic acid solution measured by the analyzing unit 8 and the quantity of the existing glyoxylic acid. The copper plating solution control unit 19 performs these  
15       calculations and controls the pump 18 according to the result of calculation. The other configuration of this embodiment is the same as that of Embodiment 13 and Embodiment 14.

As stated above, the device in accordance with the present invention can remove sulfuric and oxalic ions  
20       which deteriorate the plating characteristics as barium salts and keep an excellent plating characteristic for a long time.

[Embodiment 16]

FIG.6 is a diagrammatical sectional view of a  
25       module comprising a multi-layer wiring board 54

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produced by a copper plating method in accordance with the present invention and semiconductor elements thereon. A number 45 indicates an insulating layer.

5 The multi-layer wiring board 54 is prepared by forming a wiring pattern on each board with a known photo-resist, plating a conductor wiring 34 on the board by a method stated in said embodiments, and piling a preset number of said plated boards with an insulating layer 37 therebetween.

10 The conductor wirings on the plated boards are electrically connected by via-holes 36 and through-holes 35 which are drilled in advance and plated by a copper plating method of the present invention.

15 Semiconductor elements 46 are mounted on the predetermined locations of said multi-layer wiring board 54 by a method using solder balls 44. With this, a highly reliable module can be obtained.

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WHAT IS CLAIMED IS:

1. An electroless copper plating method using a plating solution containing copper sulfate as copper ion sources, and a copper ion complex agent, a copper ion reducing agent and a pH conditioner, wherein said method comprises steps of using the hydroxide of an alkaline earth metal as said pH conditioner to react with sulfuric ions in the electroless copper plating solution into a salt of said alkaline earth metal, removing the precipitate from the plating solution, measuring at least one of the concentration of sulfuric ion and the concentration of oxalic ion in the plating solution and keeping an optimum sulfuric ion or oxalic ion concentration during an electroless copper plating .
2. An electroless copper plating method using a plating solution containing copper sulfate as copper ion sources, and a copper ion complex agent, glyoxylic acid or salt thereof as a copper ion reducing agent, and pH conditioner, wherein said method comprises steps of using alkaline earth metal hydroxide as said pH conditioner, precipitating and removing sulfuric and oxalic ions as salts of said alkaline earth metal in the electroless plating solution during electroless copper plating .

3. An electroless copper plating machine using a plating solution containing copper sulfate as copper ion sources, and a copper ion complex agent, a copper ion reducing agent, and a pH conditioner, wherein said method comprises steps of adding at least one of alkaline earth metal, alkaline earth metal oxide, alkaline earth metal hydroxide, and alkaline earth metal salt (excluding sulfuric salt) into said plating solution, reacting with and precipitating sulfuric ions as an alkaline earth metal salt, measuring the concentration of sulfuric ions in said plating solution, and regulating the concentration thereof to a preset optimum concentration during electroless copper plating .

4. An electroless copper plating machine using a plating solution containing copper sulfate as copper ion sources, and a copper ion complex agent, glyoxylic acid or salt thereof as a copper ion reducing agent, and a pH conditioner, wherein said method comprises steps of adding at least one of alkaline earth metal, alkaline earth metal oxide, alkaline earth metal hydroxide, and alkaline earth metal salt (excluding sulfuric salt) into said plating solution, reacting with and precipitating sulfuric ions or oxalic ion as an alkaline earth metal salt during electroless copper

plating .

5. An electroless copper plating machine using a plating solution containing copper sulfate as copper ion sources, and a copper ion complex agent, glyoxylic acid or salt thereof as a copper ion reducing agent, and a pH conditioner, wherein said device comprises an electroless copper plating bath, a reaction bath which adds at least one of alkaline earth metal, alkaline earth metal hydroxide, alkaline earth metal oxide, and alkaline earth metal salt (excluding sulfuric salt) to said copper plating solution therein to react with and precipitate sulfuric ions and oxalic ion as alkaline earth metal salts in said plating solution, and a filter unit for separating said metallic salt precipitate

6. An electroless copper plating machine using a plating solution containing copper sulfate as copper ion sources, and copper ion complex agent, a copper ion reducing agent, and a pH conditioner, wherein said device comprises an electroless copper plating bath, a reaction bath which adds at least one of alkaline earth metal, alkaline earth metal hydroxide, alkaline earth metal oxide, and alkaline earth metal salt (excluding sulfuric salt) to said copper plating solution therein to react with and precipitate

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sulfuric as an alkaline earth metal salt in said  
plating solution, a filter unit for separating said  
metallic salt precipitate, means for measuring the  
concentration of sulfuric ion in said plating  
5 solution), and means for comparing said measured  
concentration by a preset reference concentration and  
controlling the quantity of said alkaline earth metal,  
alkaline earth metal hydroxide, alkaline earth metal  
oxide, or alkaline earth metal salt (excluding  
10 sulfuric salt) to be added.

7. An electroless copper plating machine using  
a plating solution containing copper sulfate as copper  
ion sources, and a copper ion complex agent, glyoxylic  
acid or salt thereof as a copper ion reducing agent,  
15 and a pH conditioner, wherein said device comprises an  
electroless copper plating bath, a reaction bath which  
adds at least one of alkaline earth metal, alkaline  
earth metal hydroxide, alkaline earth metal oxide, and  
alkaline earth metal salt (excluding sulfuric salt) to  
20 said copper plating solution therein to react with and  
precipitate sulfuric as an alkaline earth metal salt  
in said plating solution, a filter unit for separating  
said alkaline earth metal salt precipitate, means for  
measuring at least one of the sulfuric ion  
25 concentration and the oxalic ion concentration and

means for comparing at least one of said measured  
sulfuric and oxalic concentrations by a preset  
reference concentration and controlling the quantity  
of said alkaline earth metal, alkaline earth metal  
5 hydroxide, alkaline earth metal oxide, or alkaline  
earth metal salt (excluding sulfuric salt) to be added.

8. An electroless copper plating machine using  
a plating solution containing metallic ions, an agent  
for reducing said metallic ions, and a pH conditioner,  
10 wherein said device comprises an electroless copper  
plating bath, a reaction bath adding a metal or a  
compound containing a metal to said plating solution  
to precipitate ions which suppress generation of said  
plating metal as metal salts, and a ultra filtration  
15 unit for removing said metal salt precipitate.

9. An electroless copper plating machine in  
accordance with Claim 5 through Claim 8, wherein said  
filtration unit is a cross-flow type ultra filtration  
unit or a filter press type ultra filtration unit.

20 10. A multi-layer wiring board having insulating  
layers and circuit layers accumulated and cemented  
alternately whose circuit layers are electrically  
connected by copper-plated through-holes which pass  
through the insulating layer between said circuit  
25 layers or by copper-plated via-holes whose one end is

closed, wherein said plating is made by An electroless  
copper plating method in accordance with Claim 1  
through Claim 4.

11. A module having one or more semiconductor  
5 elements on said multi-layer wiring board in  
accordance with Claim 10.

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ABSTRACT

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The main purpose of the present invention is to provide a method of removing plating blocking ions such as anions in pairs with copper ions and oxidant ions of the copper ion reducing agent from the electroless copper plating solution and keeping a constant salt concentration in the electroless copper plating solution during plating, a device to realize said method, and applications thereof.

10 For An electroless copper plating method, a device thereof, and application thereof, using a plating solution containing copper sulfate as copper ion sources, and a copper ion complexing agent as copper ion sources, glyoxylic acid as a copper ion reducing agent, and pH conditioner, the present invention is characterized by precipitating and removing sulfuric and oxalic ions in said electroless copper plating solution and keeping an optimum concentration of at least one of sulfuric and oxalic ions in said electroless copper plating solution during plating.

15  
20



FIG. 1

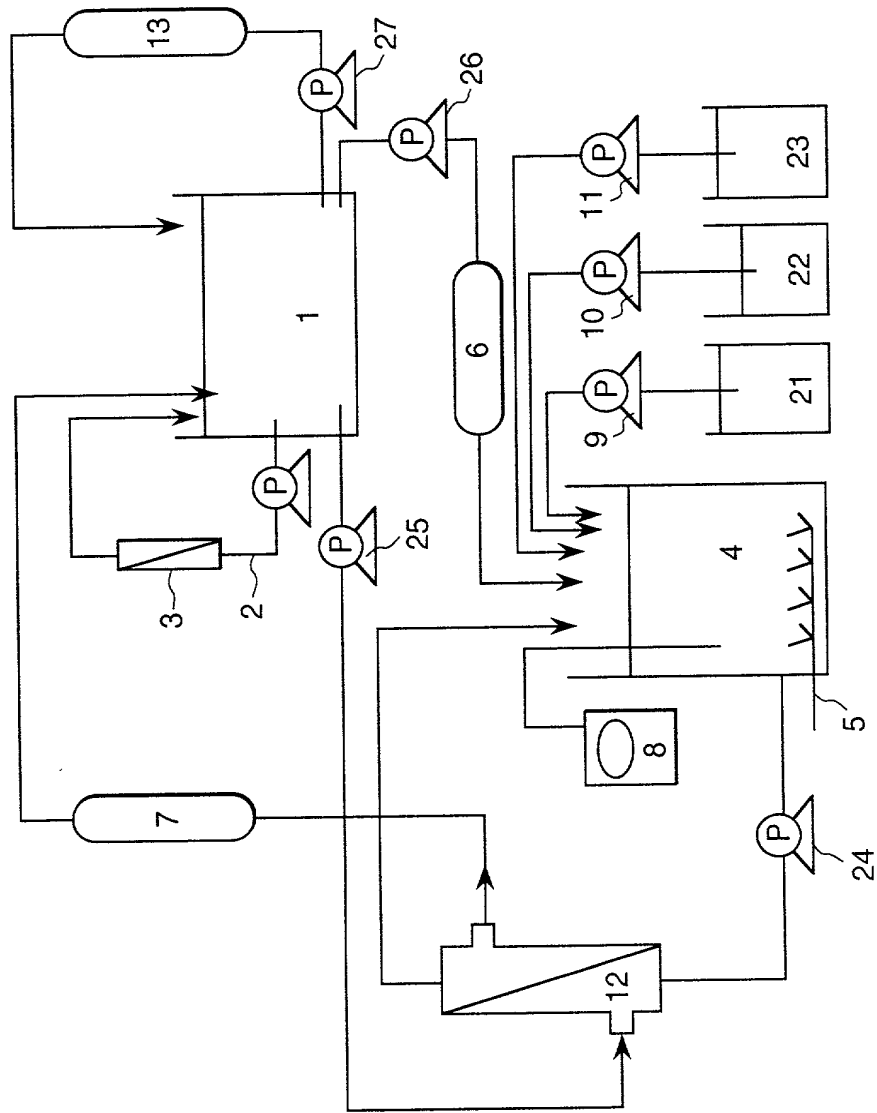


FIG. 2

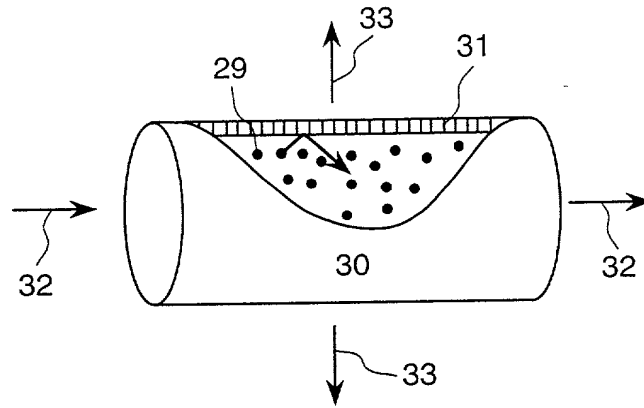
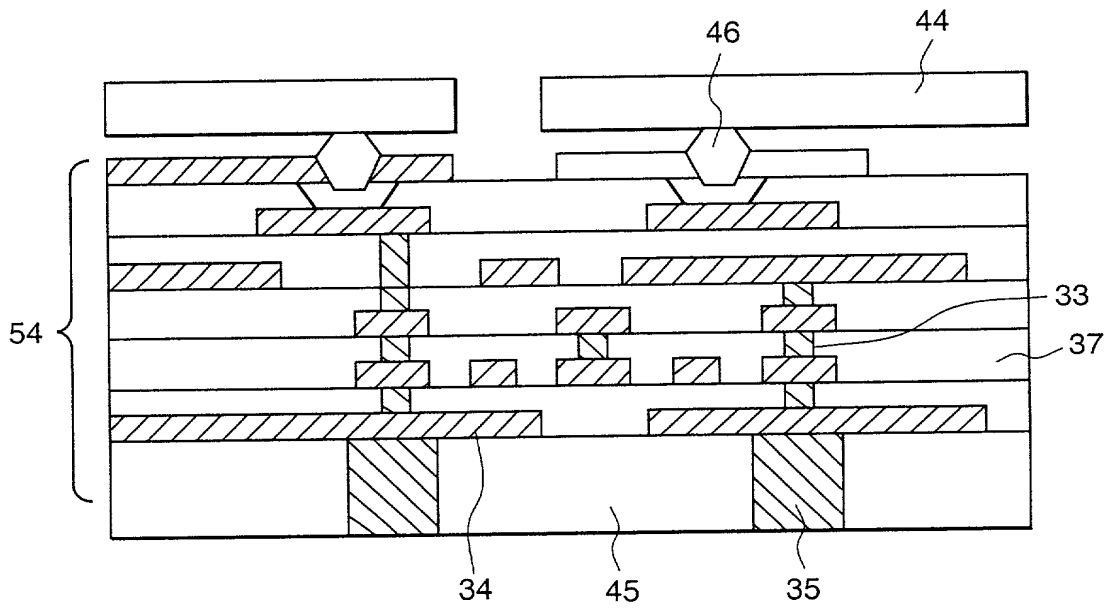


FIG. 6



**FIG. 3**

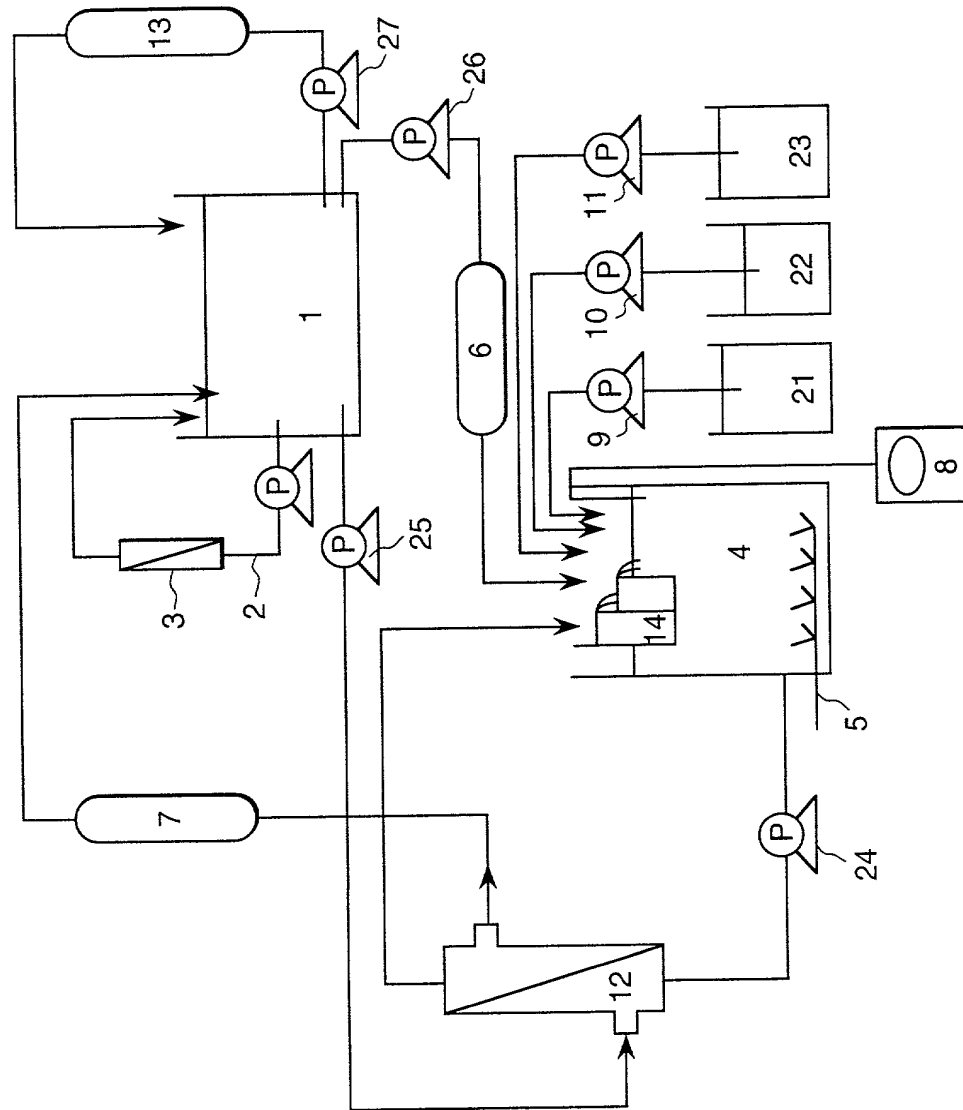
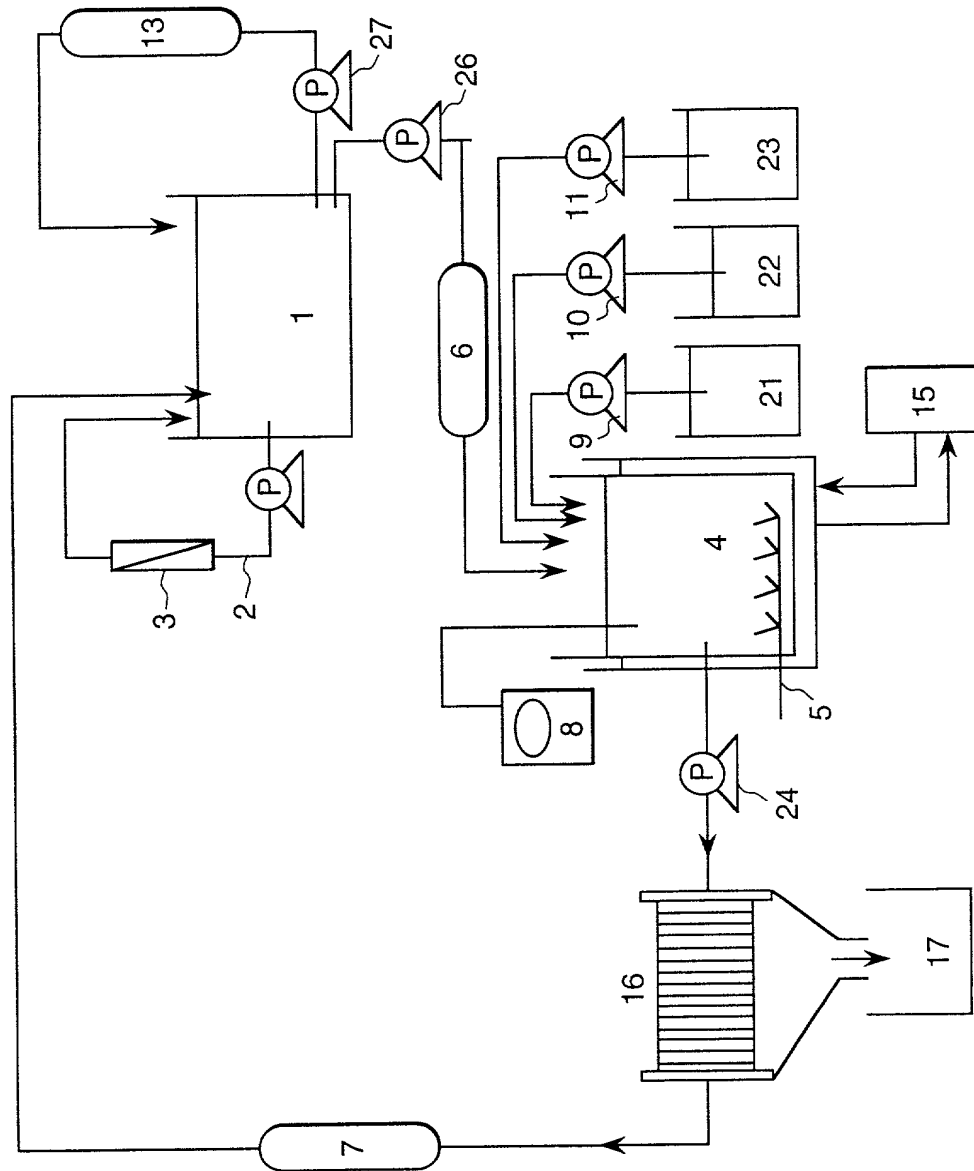


FIG. 4



**FIG. 5**

